

Internal curing of cement pastes by superabsorbent polymers studied by means of neutron radiography

SNOECK Didier^{1,a *}, ALDERETE Natalia^{1,2,b}, VAN BELLEGHEM Bjorn^{1,3,c},
VAN DEN HEEDE Philip^{1,3,d}, VAN TITTELBOOM Kim^{1,e} and DE BELIE Nele^{1,f}

¹ Magnel Laboratory for Concrete Research, Faculty of Civil Engineering and Architecture, Ghent University, Technologiepark-Zwijnaarde 904, 9052 Ghent, Belgium

² LEMIT and CONICET, 52 entre 121 y 122 s/n, La Plata 1900, Argentina

³ Strategic Initiative Materials (SIM vzw), project ISHECO within program SHE, Technologiepark-Zwijnaarde 935, 9052 Ghent, Belgium

^a didier.snoeck@ugent.be, ^b nataliamariel.alderete@ugent.be,

^c bjorn.vanbelleghem@ugent.be, ^d philip.vandenheede@ugent.be,

^e kim.vantittelboom@ugent.be, ^f nele.debelie@ugent.be

*corresponding author

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Abstract.

Autogenous shrinkage is a problem in cementitious materials with a low water-to-binder ratio. When the internal relative humidity decreases due to the ongoing hydration reaction and self-desiccation, autogenous shrinkage takes place if no external or internal water source is present. This may lead to cracking and eventually cause durability problems in constructions. Ideally, the internal relative humidity should be maintained during hydration of the cement paste. Superabsorbent polymers (SAPs) may be used to mitigate autogenous shrinkage. When self-desiccation occurs, these polymers will release their absorbed additional mixing water due to increasing capillary forces to stimulate internal curing. This release of water towards the cementitious matrix and the effect on the cementitious matrix itself can be studied by means of neutron radiography. In this study, thin samples of cement paste were casted between glass plates and the evolution of the internal water amount was studied as a function of time. In specimens without SAPs and a water-to-binder ratio of 0.30, shrinkage was seen. Furthermore, autogenous shrinkage was reduced in cement pastes when using SAPs and an additional entrained water-to-binder ratio of 0.054. The release of water from smaller SAPs (100 µm dry size) seemed to be more promising compared to bigger SAPs (500 µm) with the same absorption properties. The technique of neutron radiography supports the findings of shrinkage tests where SAPs were already proven to be useful. This opens additional insights towards the application of SAPs in the construction area.

Introduction

Autogenous shrinkage is the result of reducing distances between the solid particles in a cementitious matrix. This is due to capillary forces originating from the formed menisci and exerted hydrostatic tension forces. As cement starts to react with water, the hydration products will start to precipitate between the solid particles and water will be consumed. The remaining water in the small capillaries then exerts high hydrostatic tension forces. This induces a drop in relative humidity, the so-called self-desiccation. This leads to autogenous shrinkage.

Due to the self-desiccation and the occurring autogenous shrinkage, micro- and macro-cracks may form, especially when the water-to-cement ratio is low. These cracks impair the durability and the overall strength of the material. Consequently, this cracking should ideally be avoided.

This can be overcome by counteracting the self-desiccation by providing an internal or external water source and autogenous shrinkage could be mitigated. In this paper, the focus lies on internal

curing by means of superabsorbent polymers (SAPs) [1-5]. SAPs are an interesting material which can absorb a huge amount of fluids. They can absorb up to several hundreds of times their weight in water. This is due to osmotic pressure as the polymers contain large polymeric chains interconnected at distinct points by means of crosslinks. The chains expand upon ingress of fluids and thus results in a volumetric increase. They are mostly used in the hygiene industry or for medical purposes, but are also found in cementitious materials. They hold the water and release it towards the cementitious matrix when the relative humidity starts to drop. This will lead to the so-called internal curing, mitigating autogenous shrinkage. Besides mitigation of autogenous shrinkage, they can be used in cementitious materials for increasing the freeze/thaw resistance [6-8], for self-sealing [9-11] and for self-healing [12-15], amongst others.

In this paper, the autogenous strain is monitored in time by means of neutron radiography measurements. By using thermalized neutrons in neutron radiography, hydrogen attenuates more compared to materials like cementitious materials. It is thus an excellent tool to visualize the water and its movement in a cementitious material.

In literature, the volume change of big SAPs (several millimetres in size) used for internal curing was already studied by means of neutron radiography [16]. It proved to be a very good way to study the release of water from – in the mentioned research however very big (up to several mm) – superabsorbent polymers. The SAPs needed to be big enough to study the release of water from the SAPs with good resolution. As neutron radiography is a powerful tool to study the water movement in cementitious materials, the samples however need to be small enough to ensure good resolution of the radiographs. One other recent study [17] uses SAPs with a size in the range of mm and a clear desorption of the SAP was monitored in time. Here, in this research, the smaller SAPs (100 – 500 μm) used in practice are studied.

By using neutron radiography, interesting information about the kinetics of water release by the smaller SAPs can be obtained and this is subject of this paper.

Materials and Methods

Materials. A cement paste with a water-to-cement ratio (W/C) of 0.3 was made (R0.30). The cement used was CEM I 52.5 N (chemical composition in [4]). A reference mixture with W/B = 0.354 to study the differences in self-desiccation was also prepared: R0.35.

The dosage of the superplasticizer was kept constant, to limit its influence on the setting and hydration properties as most superplasticizers cause retardation. The amount used was 0.42 m% (mass-% of binder weight) polycarboxylate superplasticizer (Glenium 51, conc. 35%, BASF). In two other mixtures, SAPs were added in addition (A_e and B_e), as well as additional water to be absorbed to induce internal curing. Theoretically, an amount of $(W/B)_e = 0.054$ is needed to effectively mitigate autogenous shrinkage in cement pastes with a W/B = 0.30 [1, 18]. That is why the two afore-mentioned reference mixtures R0.30 and R0.35 were studied.

Two types of SAP were investigated (both obtained from the company BASF). These were SAP A, a copolymer of acrylamide and sodium acrylate (particle size $100.0 \pm 21.5 \mu\text{m}$ ($n=50$)), and SAP B, a cross-linked potassium salt polyacrylate (particle size $476.6 \pm 52.9 \mu\text{m}$ ($n=50$)). Both SAPs are bulk-polymerized and consist of irregular crushed particles. All SAPs were vacuum dried in a desiccator with silica gel prior to testing or mixing in the cement paste mixture. Dry SAP particles were added to the cement and were first dry mixed to ensure a homogenous dispersion in the cement. After this dry mixing, the additional water was added together with the mixing water and superplasticizer. The mixtures are called A_e and B_e, for SAP A and SAP B, respectively. The additional ‘_e’ stands for entrained water, which was added on top. The amount of SAP to be added to receive an additional entrained water amount of $(W/B)_e = 0.054$ was 0.22 m% (mass-% of binder weight) SAP A (A_e) and 0.45 m% SAP B (B_e), respectively.

The swelling capacities of both SAPs (the mass increase between vacuum dried and saturated particles by means of a filtration test [15]) in demineralized water, tap water and cement filtrate solution (obtained by mixing 10 g CEM I 52.5 N in 100 g of demineralized water and subsequent filtration) are given in Table 1.

Table 1. Absorption capacity of SAP in de-ionised water; tap water and cement filtrate solution with their pH, absorption capacity of SAP during mixing of a cement paste, and swelling time until full saturation of particles is achieved with standard deviations.

<i>Property</i>	<i>SAP A</i>	<i>SAP B</i>
$\Delta m/m$ de-ionised water (pH = 6.5)	305.0 ± 3.7 g/g SAP	283.2 ± 2.4 g/g SAP
$\Delta m/m$ tap water (pH = 6.8)	163.9 ± 1.2 g/g SAP	148.9 ± 0.9 g/g SAP
$\Delta m/m$ cement slurry (pH = 12.8)	61.0 ± 1.0 g/g SAP	58.4 ± 1.7 g/g SAP
$\Delta m/m$ during cement paste mixing	23 g/g SAP	11 g/g SAP
Swelling time	10 ± 2 s	60 ± 5 s

The amount of mixing water absorbed during cement paste mixing was calculated from the flow values of the different mixtures, following the Standard EN 12350-5. A comparison of the flow value of mixtures with and without SAPs may tentatively be used to reflect the absorption of the SAPs in the mortar mixture. One needs to make sure that this amount is not overestimated as it may change the overall microstructure. Microscopic analysis on polished cross-sections afterwards confirmed the exact and correct amount of entrained water [4, 19].

The swelling time was determined using a vortex method [20]. It serves as a reference on how fast the SAPs are able to absorb most of their total amount of absorbable liquid. The measured time for both SAPs was fast enough to ensure complete swelling by absorption of additional mixing water during mixing and casting. If it would be slower, the absorption would continue over time and this would lead to less workable concrete and a high risk on durability issues as the overall microstructure could change.

Sample preparation. A thin mold was made and filled with cement paste (Fig. 1). It consisted of two acrylic glass plates, placed 500 μm from each other by means of aluminum spacers. The mix was poured in the container and the mixture was sufficiently flowable to ensure complete filling without any necessity of further compaction. There was almost no air visible. The whole was covered with plastic foil to avoid evaporation and to minimize contact with ambient air.

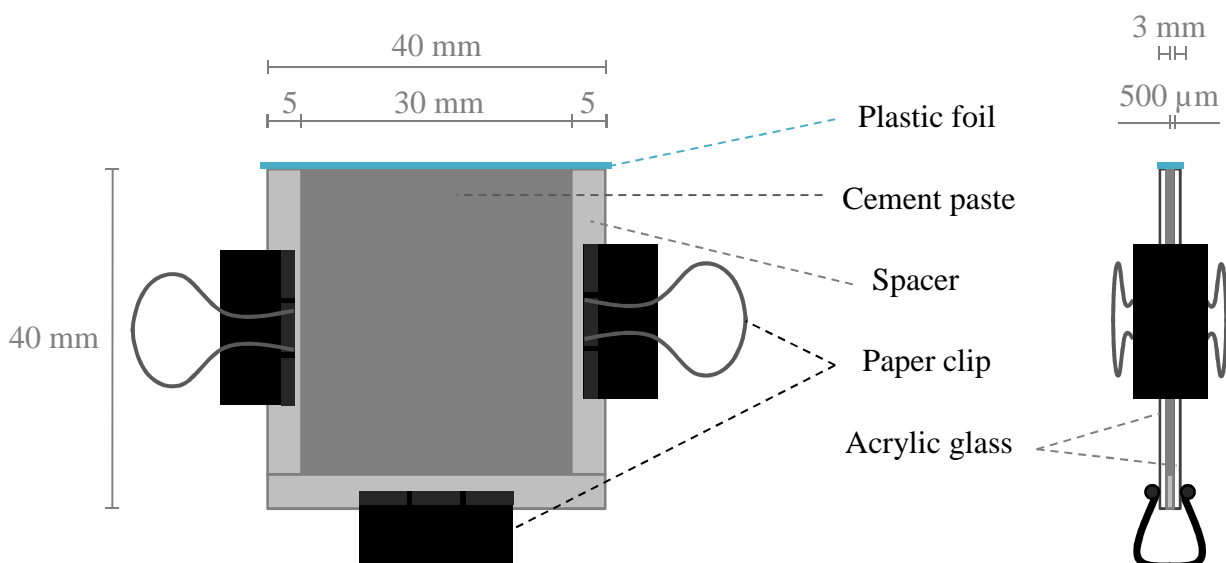


Figure 1. Schematic overview of studied sample.

Neutron radiography. The samples were quickly transferred to the neutron beam chamber and image recording began as soon as possible. The transport time was as short as experimentally and practically feasible with the aim to study the specimens as quickly as possible as the water content in the specimens and in the SAPs can change. The first measurement was taken 15 minutes after contact of the dry materials with water.

In this investigation, a neutron beam with a proton current of 1.5 mA was used at the measuring station NEUTRA, the thermal neutron radiographic facility at the Swiss spallation source SINQ of the Paul Scherrer Institute (PSI) [21]. A neutron beam travelled through the studied object, the 100 μm LiF/ZnS scintillator screen as neutron-to-light converter, hit a mirror in the dark room and was recorded by a slow-scan Andor Neo 5.5 sCMOS camera with a 50 mm AF-S NIKKOR lens. Digitization of the output of the detector resulted in an array of intensity values, corresponding to the grey values of the pixels of the obtained image. The pixel size obtained with an exposure time of 3 s was 0.273 mm/pixel. As a function of time, radiographs were made at regular time intervals to study the influence of SAPs on the cementitious matrix. The specimens were measured for a total time of 72 hours after casting.

Image analysis. Each image obtained with neutron radiography needed to be filtered with the image correction tool “Quantitative Neutron Imaging” (QNI) [22] for qualitative information. The reason for this processing is that the exponential law of attenuation is influenced by several deviations. The QNI program takes into account the CCD dark current, the background scattering, the sample scattering, the spectral effects, the intensity and the flat field correction. The program uses Monte-Carlo simulations to describe the scattering distribution of the neutron beam.

After post-processing of the radiographs, the measured time states were divided by the initial state – i.e. the first measurement – as a qualitative measurement of the moisture distribution and kinetics as a function of time. In that way, the differences in time are monitored.

To minimize the influence of the scattering of the metal paper clips in time, the region of interest was further downsized to the one depicted in Fig. 2. These regions were used in further image analysis. Also, to minimize possible influences of the sides of the sample – i.e. possible evaporation due to flaws at the edges – this region was chosen. In that way, possible changes in the cementitious matrix are studied.

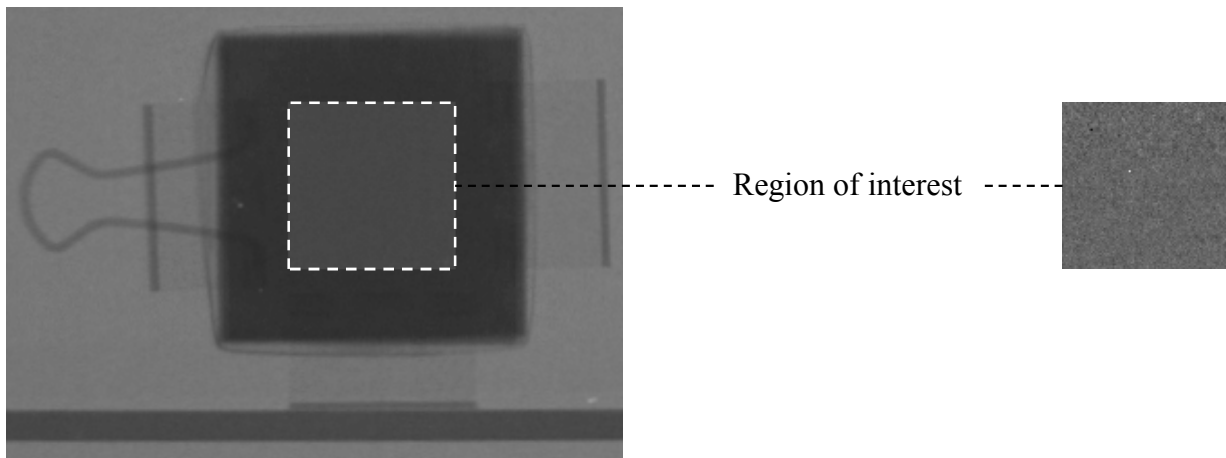


Figure 2. Studied region of interest to minimize scattering influences.

Results and discussion

The differential image series as a function of time are shown in Fig. 3. Over a total time span of 72 hours, the specimens were studied. The relative water content is represented by this grey level intensity. This was calculated with respect to the initial state by referencing each image of the time sequence to the earliest image recorded, as mentioned beforehand. The latter was performed as soon as possible, in terms of practically and experimentally most feasible. The grey level is shown with standard deviation at every time step, as the grey level of the complete region of interest was determined on five single subsequent measurements. This was done to minimize the influence of outliers and sudden intensity drops or increases of the neutron beam line. Furthermore, a trend line (dashed lines in Fig. 3) is added to show the decrease in grey values in time. The studied radiographs are also shown below the graph as examples for comparative reasons. Each pixel represents a change with respect to the reference starting radiograph.

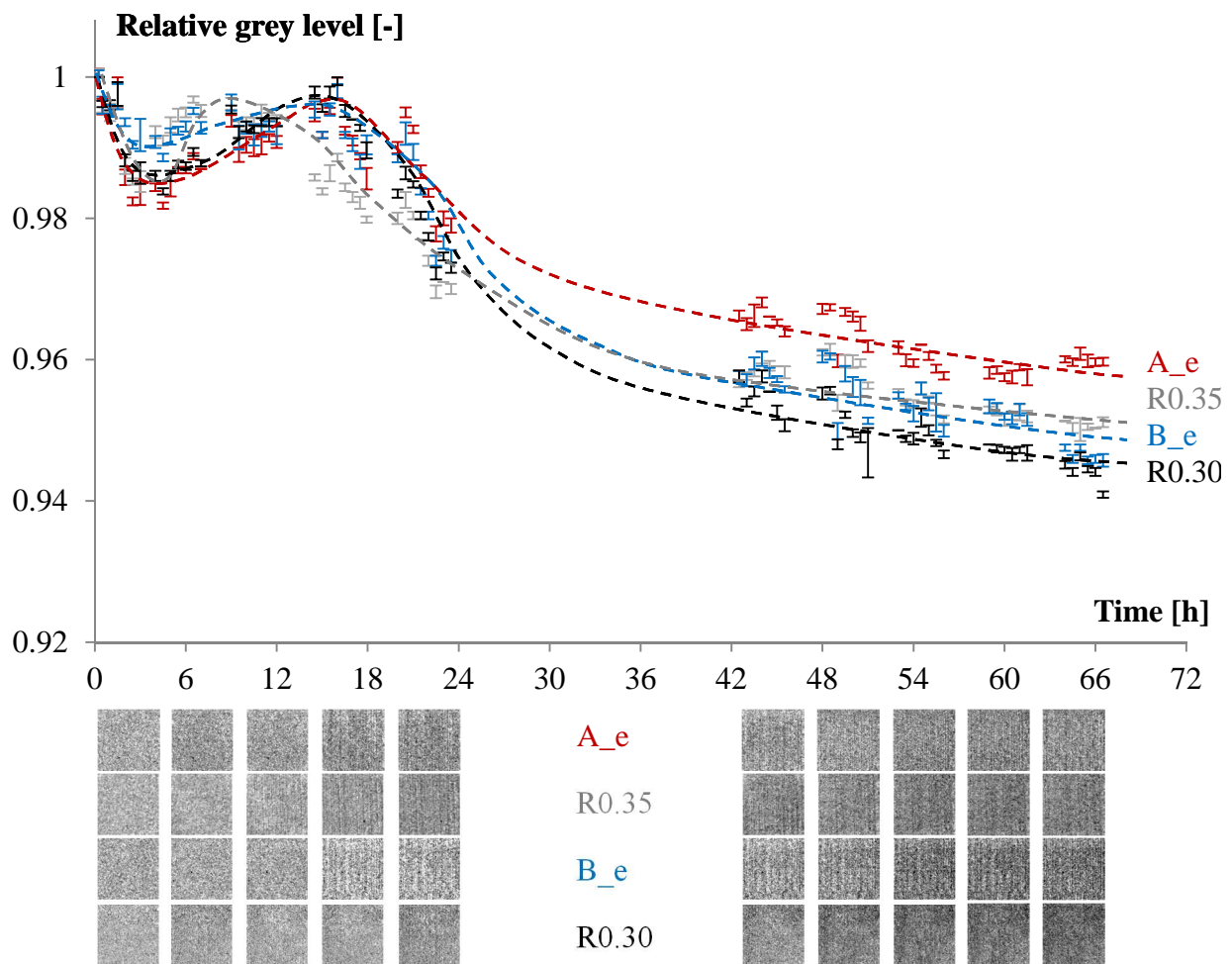


Figure 3. Grey levels, where 0 is black and 1 is white, as a function of time of the studied specimens. R0.30/0.35 states the reference sample with a water-to-cement ratio of 0.30/0.35; A_e and B_e specimens with superabsorbent polymers and entrained water for internal curing. A section of the grey neutron radiographs for every studied specimen at a respective time is shown for comparative reasons.

A decrease in relative grey level is seen, especially for the R0.30 mixture, with a water-to-cement ratio of 0.30. In systems with a water-to-cement ratio of 0.30 complete hydration is not possible. The hydration stops at a minimum porosity of the cement gel (26-28%). The capillary

water reacts until it is consumed and the cement starts to react with the harder bound gel water, causing the relative humidity to decrease and the cement paste to self-desiccate. This decrease can be seen as a sort of autogenous shrinkage.

The darker image could also point to the change in overall water content due to an exchange of moisture with the surroundings. This could indicate that the sealing was not hermetic. By using the plastic foil in a good way, and by making sure there was no leaking possible, this effect should be minimal. However, it can still be present as only tiny openings are needed for moisture exchange. However, in the interior of the material, this should not be the case. That is why the region of interest was chosen in such a way that it was not near an edge. In that way, the authors think that a contraction of the cementitious matrix was measured. As the dense cementitious material – with water in its overall presence – came closer together due to self-desiccation and autogenous shrinkage, the overall grey value should be darker. This was seen as a drop in relative grey value to lower values.

An increase in water-to-cement ratio from 0.30 to 0.354 results in a less dark image. This is due to the fact that the autogenous shrinkage in such a mixture (0.354) is lower due to the higher water-to-cement ratio. This is due to the denser matrix formed in mixtures with a lower water-to-binder ratio, increasing the hydrostatic tension forces (capillary forces) and leading to the increase in self-desiccation and autogenous shrinkage.

With an additional (entrained) water-to-cement ratio of 0.054 through pre-described water-filled SAP inclusions, internal curing takes over and the self-desiccation is mitigated. Comparing this SAP system with a plain water-to-cement ratio of 0.354, the maximum degree of hydration is the same and the overall porosity is the same as well. The difference is that in the SAP entrained system, macro pores are more numerous than the finer capillary pores present in the system without internal curing [19, 23].

When using SAPs for internal curing, this autogenous shrinkage can be overcome. As found in previous research [4], SAP A is able to completely mitigate autogenous shrinkage as for SAP B this is not entirely the case. The water in SAP B is possibly held too long for ideal mitigation of autogenous shrinkage or the larger SAP B particle is unable to transfer the water further away from the macro pore into the cementitious matrix. The water was not released too fast as the macro pores had the expected size when polished sections of the hardened material were microscopically studied [4]. A smaller SAP – the ideal swollen size is in the order of magnitude of 100-200 μm [1, 2] – is able to transfer the included water to its surroundings. This would lead to a more ideal mitigation of self-desiccation. SAP A with a size of 257 μm in swollen state is of the specific size but a swollen SAP B with a size of 981 μm on average is too big. Therefore, one should prefer SAP A over SAP B in terms of mitigating autogenous shrinkage.

In Fig. 3 it can be seen that SAP A (A_e) is able to mitigate shrinkage and SAP B (B_e) is not as efficient as SAP A in terms of internal curing. This is the same result as found when performing autogenous shrinkage tests measuring the length change of sealed corrugated tubes [4]. However, for self-sealing and self-healing, the larger SAP B particle is preferred [10, 15] as smaller SAPs could be washed out from a crack of for example 300 μm . Also, as the amounts of SAP for self-sealing and self-healing are in terms of 1 m% of cement weight and thus higher than the amounts used for mitigating autogenous shrinkage (0.2 – 0.5 m%), the influences on the microstructure and strength of specimens containing smaller SAPs are more pronounced and not ideal [19]. Whereas internal curing may increase the strength, macro pore formation causes the opposite effect. This latter effect is more pronounced when using a high water-to-cement ratio [19] as the beneficial effect of internal curing is less, compared to a lower water-to-cement ratio where autogenous shrinkage is more dominant.

Only some slight hints were seen of the relocation of water from SAPs to the cementitious matrix for internal curing. In the region of interest at the right-hand side of Fig. 2 some lighter and darker regions are seen. The darker regions may contain SAP as it contains more water compared to the cementitious matrix, which should be lighter. As the thickness of the sample container was

spaced at 500 μm and the swollen SAP size is in that order of magnitude, the SAPs should clearly be distinguishable compared to the cementitious matrix.

It was unfortunate that the resolution was not sufficient to study the SAPs and the distribution of water near the SAP boundaries. The SAP size was in the order of magnitude of the pixel resolution and several pixels need to be combined to significantly see differences. Details are therefore not easily seen and the effects of the release of water to the cementitious matrix and the SAP particles themselves were smeared. This was due to the used measuring setup and settings. The only significant result which could be obtained was the overall grey distribution of the samples. The further step in this research is to use a better setup with better resolution to study the water release by the SAPs to the cementitious matrix in more detail.

Conclusions

- Neutron radiography is a powerful non-destructive test technique to determine the water distribution in a cementitious material.
- Neutron radiography can be used to study the influences of superabsorbent polymers (SAPs) on various cementitious properties as long as the resolution is sufficient.
- The smaller SAP A is more ideal compared to the larger SAP B in terms of mitigating self-desiccation and autogenous shrinkage.
- In further research the water kinetics from the SAPs towards the cementitious matrix will be studied in more detail.

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